



# Towards heterogeneous $\text{Al}_x\text{CoCrFeNi}$ high entropy alloy via friction stir processing

Tianhao Wang, Shivakant Shukla, Mageshwari Komarasamy, Kaimiao Liu, Rajiv S. Mishra \*

Center for Friction Stir Processing and Advanced Materials Manufacturing Processes Institute, Department of Materials Science and Engineering, University of North Texas, Denton, TX 76203, USA

## ARTICLE INFO

### Article history:

Received 18 April 2018

Received in revised form 25 October 2018

Accepted 28 October 2018

Available online 29 October 2018

### Keywords:

High entropy alloy

Heterogeneous

Friction stir processing

Strength

Ductility

## ABSTRACT

A heterogeneous bimodal-grained  $\text{Al}_x\text{CoCrFeNi}$  high entropy alloy was realized through friction stir processing (FSP) with the addition of Al powders. With the bimodal-grained structure and second phases, strength was increased and ductility was retained as compared with the friction stir processed base alloy. Face-centered cubic grains in the matrix were refined from  $\sim 500\ \mu\text{m}$  to  $\sim 15\ \mu\text{m}$  by FSP and subsequent recrystallization. With addition of Al powders, localized Al-rich regions facilitated the formation of body-centered cubic phase (Al, Ni-rich) and Al rich precipitates, which further refined grain size to  $\sim 5\ \mu\text{m}$  and enhanced local strength.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Since most metals conform to the strength-ductility trade-off principle, a combination of high strength and adequate ductility is not easily accessible [1,2]. To overcome this paradigm, researchers have designed multi-component and multiphase alloys [3] as well as composites [4] to achieve high strength – ductility combination. Recently, a novel design towards strength-ductility synergy was proposed by deploying heterogeneous structures [5], which include,

- bimodal-grained Cu produced by cryogenic rolling followed by secondary crystallization [6],
- harmonic structure of Cu fabricated through mechanical milling or high-energy ball milling followed by spark plasma sintering or hot roll sintering [7],
- heterogeneous lamellar structure of Ti produced via asymmetric rolling and partial recrystallization [8], and
- gradient-grained Cu achieved by surface mechanical attrition and surface mechanical grinding treatments [9].

All heterogeneous structures mentioned above feature a favorable combination of higher strength and ductility compared with their homogeneous counterparts.

Facilitating an ultrafine-grained structure via a deformational process was the initial step for heterogeneous microstructure

fabrication. Friction stir processing (FSP), a well-known microstructural modification method, has been applied for fabrication of ultrafine-grained Al alloys [10] and steel [11]. Compared with the deformation based methods applied in previous studies [6–9], FSP involves high-temperature severe plastic deformation and promotes formation of fine recrystallized grains in a single step. Furthermore, FSP can be applied for heterogeneous bulk material, whereas the other deformation based methods cannot. The introduction of additional material during FSP to produce nano composites on aluminum alloys [12,13] can be regarded as one kind of heterogeneity. Therefore, FSP is a promising candidate method for producing heterogeneous-structure metallic materials.

High entropy alloys (HEAs) are nearly equi-atomic and multi-principal element systems, and are naturally heterogeneous in atomic distribution [14,15]. Single-phase HEAs include face-centered cubic (FCC) HEAs or body-centered cubic (BCC) HEAs or hexagonal close packed (HCP) HEAs. Generally, FCC HEAs obtain higher ductility but lower strength compared with HCP and BCC HEAs [16]. In this study, as-cast  $\text{Al}_{0.1}\text{CoCrFeNi}$  HEA, which has a single FCC phase, was processed by FSP with additional Al powders. Strength was enhanced via grain refinement and second-phase precipitation, while maintaining ductility because of its heterogeneous structure.

## 2. Experimental

Holes with diameter of 1.2 mm, depth of 3.8 mm and gap of 2.5 mm along the tool traverse direction were introduced via

\* Corresponding author.

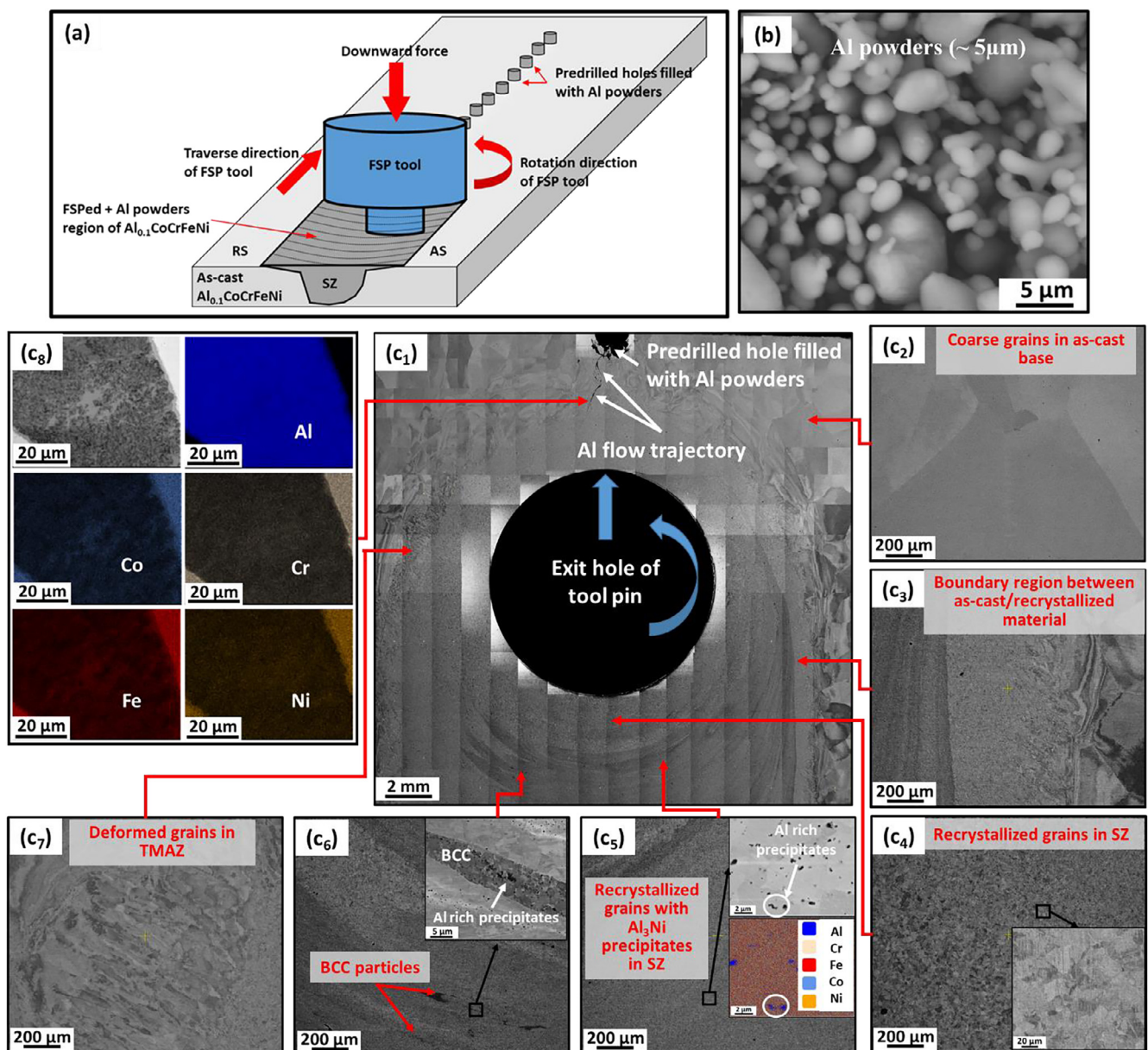
E-mail address: [Rajiv.Mishra@unt.edu](mailto:Rajiv.Mishra@unt.edu) (R.S. Mishra).

drilling on the as-cast  $\text{Al}_{0.1}\text{CoCrFeNi}$  plates ( $\sim 6.0$  mm thick) (Fig. 1(a)). Al powders of 99.9% purity and  $\sim 5$   $\mu\text{m}$  average particle size (Fig. 1(b)) were filled into these holes. A W-Re based FSP tool was used for processing. Pin length, pin diameter at root and tip, and shoulder diameter were 3.8 mm, 7.6 mm, 5.0 mm, and 16.0 mm, respectively. Tool rotation rate of 600 rotations per min (rpm) and traverse speed of 50.4 mm per min were followed. The rotating tool was traversed along the holes filled with Al powders (Fig. 1(a)). Note that the volume percentage of holes to processed region was  $\sim 18\%$ . Horizontal and transverse cross sections of friction stir processed (FSPed) volume were cut by electrical discharge machining and were final polished to 0.02  $\mu\text{m}$  surface finish with colloidal silica suspension. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and electron backscattered diffraction (EBSD) analyses were carried out using FEI Nova NanoSEM 230 with EDAX Octane Elite EDS. Mini-tensile testing

of as-cast material, FSPed and FSPed + Al powders specimens was conducted at an initial strain rate of  $0.001 \text{ s}^{-1}$ . The width, thickness and gage length of the samples were 1.0, 1.0, and 2.0 mm, respectively. Detail of the mini-tensile testing specimen used in this study was depicted in a previous work [17]. Five samples were tested for each condition.

### 3. Results and discussion

Al powders in the holes created composition heterogeneity in the processed volume, which in turn induced grain size heterogeneity. The complete formation process of the heterogeneous microstructure was observed on the horizontal section of FSPed material around the exit hole (Fig. 1(c<sub>1-8</sub>)). During FSP of  $\text{Al}_{0.1}\text{-CoCrFeNi}$  with Al powders, Al powders first melted due to high temperature ( $>800^\circ\text{C}$  [18]) and then moved along with the



**Fig. 1.** (a) schematic of FSP on the as-cast  $\text{Al}_{0.1}\text{CoCrFeNi}$  plate along with Al powders in the predrilled holes, (b) as-received Al powders, (c<sub>1</sub>) horizontal section of FSPed sample at the exit hole, (c<sub>2</sub>) coarse grains in the as-cast base alloy, (c<sub>3</sub>) boundary region between as-cast/recrystallized zone showing gradient-grained structure, (c<sub>4</sub>) recrystallized grains without Al rich precipitates in the SZ, (c<sub>5</sub>) recrystallized grains with Al rich precipitates in the SZ, (c<sub>6</sub>) band regions with BCC phase and Al rich precipitates in the SZ, (c<sub>7</sub>) deformed grains in TMAZ and (c<sub>8</sub>) EDS mapping on the Al flow trajectory showing that Al melted and the other elements reacted with it.

deforming base material (Fig. 1(c<sub>1</sub>)). The movement led to the intermixing of Al and other elements such as Co, Cr, Fe and Ni, as clearly shown in the EDS mapping of the Al-rich region (Fig. 1(c<sub>8</sub>)). With continued intermixing and deformation, the localized Al-rich region transformed to either Al-rich (Fig. 1(c<sub>5</sub>)) or Al-Ni rich (BCC structure) phases (Fig. 1(c<sub>6</sub>)). Moreover, further deformation and subsequent reaction of BCC phase were possibilities that might lead to the formation of Al-rich phase. EDS mapping presented in the inset of Fig. 1(c<sub>5</sub>) shows the existence of Al-rich phases. The Al-rich phase is likely to be Al<sub>3</sub>Ni according to Komarasamy et al. [19]. Furthermore, the presence of Al rich precipitates had significantly reduced the FCC grain size (Fig. 1(c<sub>5</sub>)), while the processed region without Al rich precipitates exhibited a coarser FCC grain size (Fig. 1(c<sub>4</sub>)). Note the extremely coarse grain structure of the as-cast material (Fig. 1(c<sub>2</sub>)) and gradient-grained structure at the boundary region between as-cast and processed material (Fig. 1(c<sub>3</sub>)). Thus, the processed volume consisted of recrystallized regions of (a) purely Al<sub>0.1</sub>CoCrFeNi and (b) Al-rich regions featuring BCC, Al rich precipitates, and finer FCC phase. Overall, the processed volume was comprised of a fine-grained region with second phases and a coarse-grained region without additional phases, both of which led to heterogeneity in two microstructural elements.

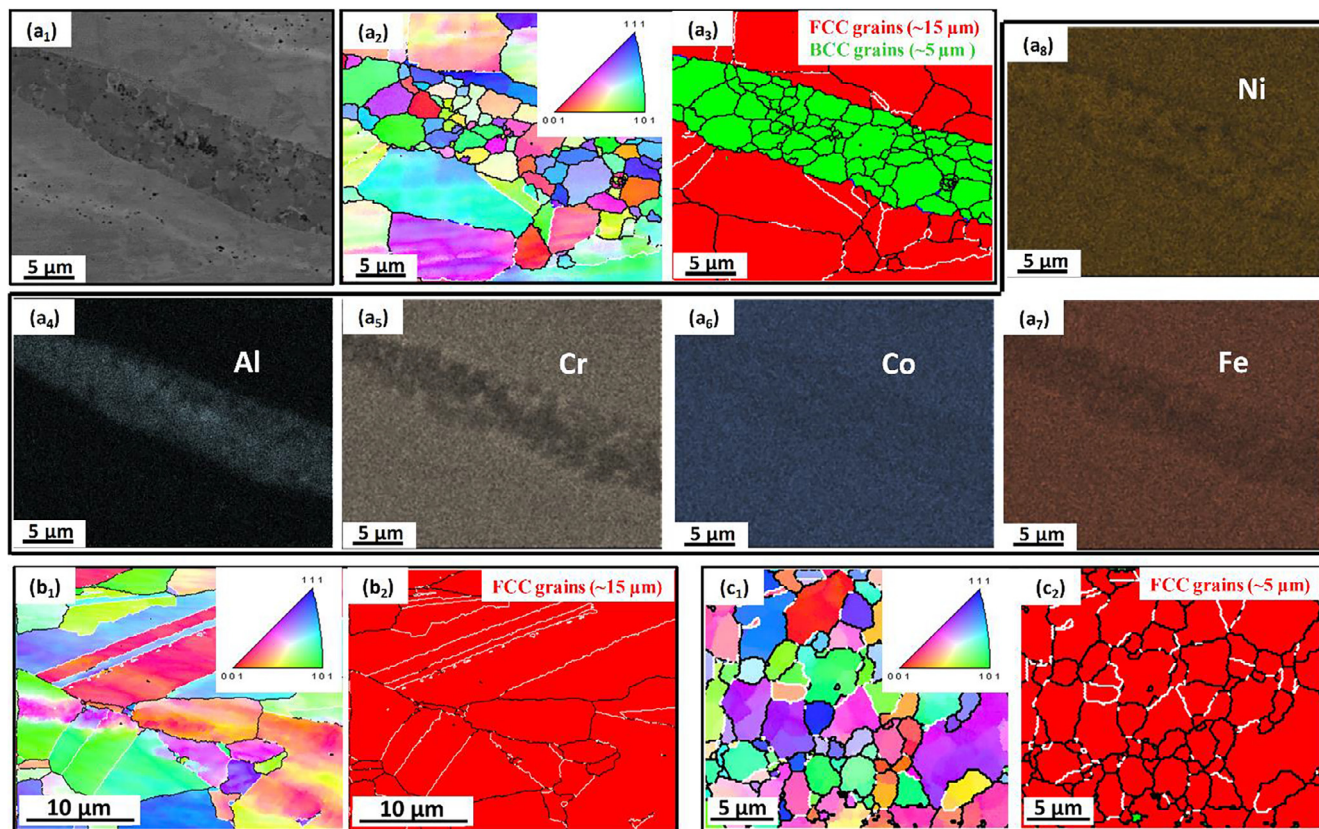
In summary, the localized Al-rich region had three different statuses: (1) predrilled holes with Al powders (before FSP), (2) Al powders melting with Co, Cr, Fe and Ni reacting to it (initial stage of FSP) and (3) BCC phase and Al rich precipitate out locally (following stage of FSP). Al rich precipitates are observed in the BCC (Fig. 2(a<sub>1</sub>)). EBSD (Fig. 2(a<sub>2,3</sub>)) of this region confirms that BCC phase has finer grain size than the surrounding FCC grains. EDS mapping (Fig. 2(a<sub>4-8</sub>)) of this region shows that Al and Ni are

rich in the BCC phase region, Co is homogeneous in BCC and FCC, Fe is deprived in BCC, and Cr is richer at the BCC/FCC boundaries. In addition, Al rich precipitates in BCC phase have the highest Al contents. Recrystallized FCC grain sizes can reach ~15 μm without Al rich precipitates (Fig. 2(b<sub>1,2</sub>)). Recrystallized FCC grain size is reduced to ~5 μm due to precipitation of Al rich particles (Fig. 2(c<sub>1,2</sub>)). Twins are observed in the recrystallized FCC grains (white lines in Fig. 2(a<sub>3</sub>, b<sub>2</sub>, c<sub>2</sub>)).

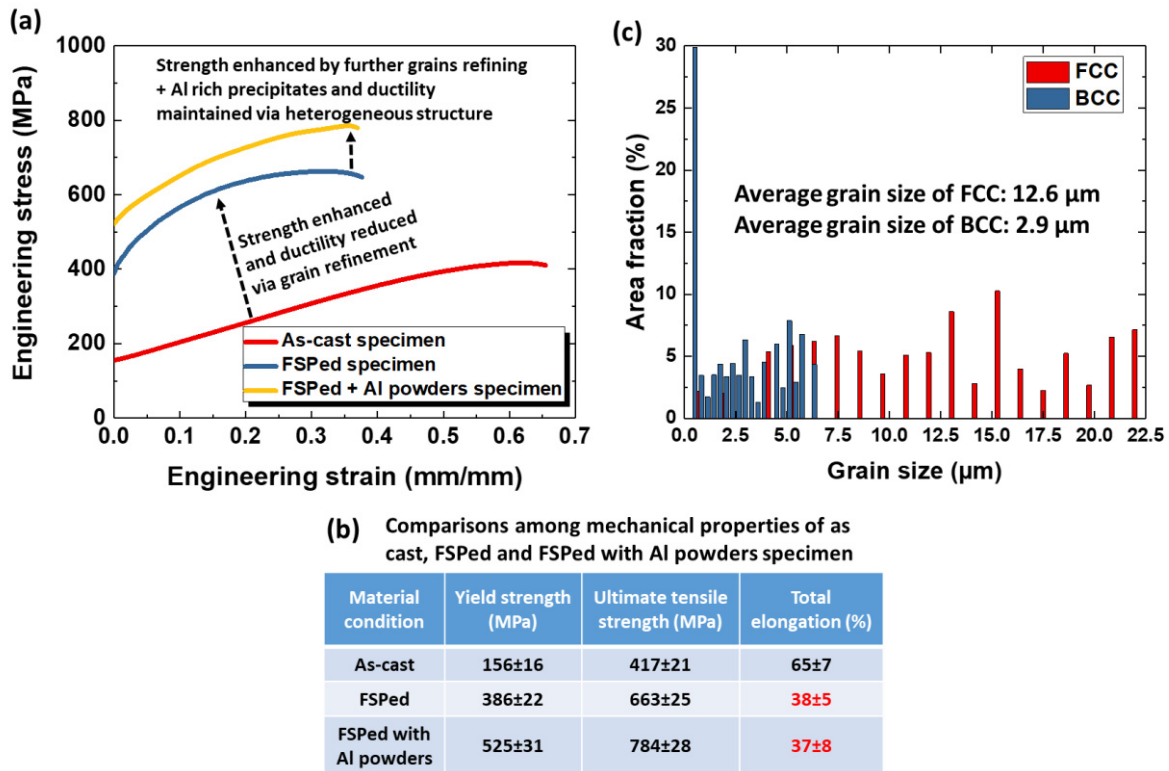
Tensile properties of the as-cast, FSPed, and FSPed + Al powders specimens confirmed that FSP increased strength but resulted in reduced ductility as compared with the as-cast material (Fig. 3(a)). This reduced ductility was due to grain refinement and its negative impact on dislocation storage. Interestingly, FSP of Al<sub>0.1</sub>CoCrFeNi with Al powders increased yield strength further by 130 MPa, but retained the ductility as compared with FSPed specimen without Al addition. The localized Al-rich region facilitated the formation of Al rich precipitates, which further refined FCC grains and enhanced strength. Ultimate tensile strength, yield strength and total elongation of as-cast, FSPed, and FSPed + Al powders specimen are listed to compare (Fig. 3(b)).

#### 4. Conclusions

- (1) Heterogeneous structures of bimodal-grained Al<sub>x</sub>CoCrFeNi were obtained via FSP with addition of Al powders. FSP enhanced strength and reduced ductility through grain refinement. FSP with addition of Al powders further increased strength by supplementary grain refinement and formation of second phase precipitates, and retained ductility through bimodal-grained structure as compared with FSPed specimen without Al addition.



**Fig. 2.** Microstructure observation in the SZ of the FSPed + Al powders specimen: (a<sub>1</sub>) SEM micrograph, (a<sub>2</sub>) IPF map and (a<sub>3</sub>) phase map, (a<sub>4-8</sub>) EDS mapping on the BCC region, (b<sub>1</sub>) IPF map, (b<sub>2</sub>) phase map of recrystallized FCC region without Al rich precipitates, (c<sub>1</sub>) IPF map and (c<sub>2</sub>) phase map of recrystallized FCC region with Al rich precipitates.



**Fig. 3.** (a) Stress-strain curves of as cast, as FSPed and FSPed with Al powders, (b) mechanical property comparisons among as cast, FSPed and FSPed with Al powders specimen, and (c) distribution of grain size for FCC and BCC phases.

- (2) The evolution of localized Al-rich region during FSP was clarified as melting of Al powders and reaction with Co, Cr, Fe and Ni to produce regions with BCC phase and Al rich precipitates.

## Acknowledgments

The authors gratefully acknowledge the support of National Science Foundation (NSF) grant 1435810. Authors also thank the Materials Research Facilities (MRF) at University of North Texas for the use of microscopy equipment.

## References

- [1] C. Koch, D. Morris, K. Lu, A. Inoue, Ductility of nanostructured materials, *MRS Bull.* 24 (1999) 54–58.
- [2] Y.T. Zhu, X. Liao, Nanostructured metals: retaining ductility, *Nat. Mater.* 3 (2004) 351.
- [3] K. Kumar, H. Van Swygenhoven, S. Suresh, Mechanical behavior of nanocrystalline metals and alloys, *Acta Mater.* 51 (2003) 5743–5774.
- [4] U.G. Wegst, H. Bai, E. Saiz, A.P. Tomsia, R.O. Ritchie, Bioinspired structural materials, *Nat. Mater.* 14 (2015) 23.
- [5] X. Wu, Y. Zhu, Heterogeneous materials: a new class of materials with unprecedented mechanical properties, *Mater. Res. Lett.* 5 (2017) 527–532.
- [6] Y. Wang, M. Chen, F. Zhou, E. Ma, High tensile ductility in a nanostructured metal, *Nature* 419 (2002) 912.
- [7] C. Sawangrat, S. Kato, D. Orlov, K. Ameyama, Harmonic-structured copper: performance and proof of fabrication concept based on severe plastic deformation of powders, *J. Mater. Sci.* 49 (2014) 6579–6585.
- [8] X. Wu, M. Yang, F. Yuan, G. Wu, Y. Wei, X. Huang, et al., Heterogeneous lamella structure unites ultrafine-grain strength with coarse-grain ductility, *Proc. Natl. Acad. Sci. U.S.A.* 112 (2015) 14501–14505.
- [9] Lu.K. Nanomaterials, Making strong nanomaterials ductile with gradients, *Science* 345 (2014) 1455–1456.
- [10] Y. Kwon, N. Saito, I. Shigematsu, Friction stir process as a new manufacturing technique of ultrafine grained aluminum alloy, *J. Mater. Sci. Lett.* 21 (2002) 1473–1476.
- [11] R. Ueji, H. Fujii, L. Cui, A. Nishioka, K. Kunishige, K. Nogi, Friction stir welding of ultrafine grained plain low-carbon steel formed by the martensite process, *Mater. Sci. Eng.: A* 423 (2006) 324–330.
- [12] A. Shafiei-Zarghani, S. Kashani-Bozorg, A. Zarei-Hanzaki, Microstructures and mechanical properties of Al/Al<sub>2</sub>O<sub>3</sub> surface nano-composite layer produced by friction stir processing, *Mater. Sci. Eng.: A* 500 (2009) 84–91.
- [13] C. Hsu, P. Kao, N. Ho, Ultrafine-grained Al–Al<sub>2</sub>Cu composite produced in situ by friction stir processing, *Scr. Mater.* 53 (2005) 341–345.
- [14] J. Yeh, S. Chen, S. Lin, J. Gan, T. Chin, T. Shun, et al., Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes, *Adv. Eng. Mater.* 6 (2004) 299–303.
- [15] J. Yeh, S. Lin, T. Chin, J. Gan, S. Chen, T. Shun, et al., Formation of simple crystal structures in Cu–Co–Ni–Cr–Al–Fe–Ti–V alloys with multiprincipal metallic elements, *Metall. Mater. Trans. A* 35 (2004) 2533–2536.
- [16] Y. Lu, Y. Dong, S. Guo, L. Jiang, H. Kang, T. Wang, et al., A promising new class of high-temperature alloys: eutectic high-entropy alloys, *Sci. Rep.* 4 (2014) 6200.
- [17] M. Komarasamy, R.S. Mishra, Serration behavior and shear band characteristics during tensile deformation of an ultrafine-grained 5024 Al alloy, *Mater. Sci. Eng.: A* 616 (2014) 189–195.
- [18] L. Cui, H. Fujii, N. Tsuji, K. Nogi, Friction stir welding of a high carbon steel, *Scr. Mater.* 56 (2007) 637–640.
- [19] M. Komarasamy, T. Wang, K. Liu, L. Reza-Nieto, R.S. Mishra, Hierarchical microstructure for exceptional strength-ductility combination in a complex concentrated alloy, *Scr. Mater.* (2018), in press.